

# PATENT SPECIFICATION

NO DRAWINGS

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International Classification:—A01n. C07c.

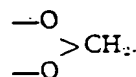
## COMPLETE SPECIFICATION

### Herbicidal Compositions and Novel Compounds for use therein

We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C.3, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with compositions for use as herbicides. This invention is also concerned with novel compounds having herbicidal properties for use in said compositions and to a process for preparing said novel compounds.

The compositions of the invention comprise a benzonitrile derivative having the general formula



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In the above formula, the halogen is preferably chlorine or bromine. Preferably at least one of X and Y represent a halogen atom.

The acyl group which R and R<sup>1</sup> may represent is the radical of a carboxylic acid which may be acyclic or cyclic and saturated or unsaturated. Preferred acids are aliphatic carboxylic acids of 1 to 4 carbon atoms, especially acetic acid.

The following are examples of active compounds of the above general formula which among others can be used in the compositions of the invention:

- 3 - hydroxy - 2 - chlorobenzonitrile
- 3 - hydroxy - 2,6 - dichlorobenzonitrile
- 3 - acetoxy - 2 - chlorobenzonitrile
- 3 - acetoxy - 2,6 - dichlorobenzonitrile
- 3 - butyryloxy - 2,6 - dichlorobenzonitrile
- 3 - hydroxy - 2,4,6 - trichlorobenzonitrile
- 3,6 - dihydroxy - 2 - cyanobenzonitrile
- 3 - phenoxy - 2,4,6 - trichlorobenzonitrile
- 3 - carboxymethoxy - 2,6 - dichlorobenzonitrile and its ethyl ester
- 3,6 - diacetoxy - 2 - chlorobenzonitrile
- 3,6 - diacetoxy - 2,4 - dichlorobenzonitrile
- 3 - methoxy - 2,6 - dichlorobenzonitrile
- 3,4 - dimethoxy - benzonitrile
- 3,6 - dimethoxy - 2 - chlorobenzonitrile
- 3,4 - methylenedioxybenzonitrile
- 2 - chloro - 3,4 - methylenedioxybenzonitrile

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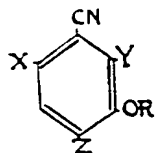
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as well as the corresponding bromo derivatives obtained by replacing one or more of the chlorine atoms by bromine atoms, and the sodium and potassium salts of the hydroxy compounds.

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Compounds of the above general formula



wherein R represents a hydrogen atom, an alkali metal, preferably sodium or potassium, an acyl group, a phenyl group, or an alkyl group of 1 to 4 carbon atoms, preferably a methyl group, which alkyl group may be substituted by a carboxyl group or by an alkoxy-carbonyl group; X represents a hydrogen atom, a halogen atom or the group OR<sup>1</sup> wherein R<sup>1</sup> represents a hydrogen atom, an alkali metal, preferably sodium or potassium, or an alkyl group of 1 to 4 carbon atoms, or an acyl group; Y represents a hydrogen atom, a halogen atom or a cyano group; Z represents a hydrogen atom, a halogen atom or an alkoxy group of 1 to 4 carbon atoms, preferably a methoxy group, or Z and OR together represent a methylene dioxy group

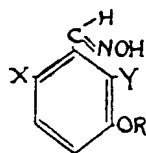
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wherein Y represents a halogen atom, X and Z each represent a hydrogen atom or a halogen atom, and R represents a hydrogen atom, a sodium or potassium atom, or a methyl or acetyl group, or in which R represents a methyl group and Z represents a methoxy group, have particularly good herbicidal activity and are preferred compounds for use in the compositions of the invention. Some of these compounds are novel. Examples of such preferred compounds are 2,4,6 - trichloro - 3 - hydroxybenzonitrile, 3,4 - dimethoxybenzonitrile and the novel compounds

- 15 2 - chloro - 3 - hydroxybenzonitrile  
2 - chloro - 3 - acetoxybenzonitrile  
2,6 - dichloro - 3 - hydroxybenzonitrile  
2,6 - dichloro - 3 - acetoxybenzonitrile

The novel compounds of the invention can be prepared by treating the correspondingly substituted 3 - hydroxybenzaldehyde or 3 - acetoxybenzaldehyde of formula



wherein X represents a hydrogen or halogen atom and Y represents a halogen atom, said halogen being chlorine or bromine, and R represents a hydrogen atom or an acetyl group, with a dehydrating agent which will remove the elements of water from the aldoxime group. Suitable dehydrating agents for this purpose are acid chlorides or acid anhydrides, especially acetyl chloride and acetic anhydride. Preferably the aldoxime and the acid chloride or acid anhydride preferably in excess, are heated together under reflux. In general, the reaction is complete in about four to five hours. Shorter reaction times may be employed but the products obtained are less pure. The re-

Analysis Found: C 46.7; H 2.3; Cl 30.7%  
C<sub>7</sub>H<sub>3</sub>O<sub>2</sub>NCl<sub>2</sub> requires C 46.9; H 2.2; Cl 30.9%

80 In other similar preparations, the product was extracted with ether from the aqueous reaction mixture.

#### EXAMPLE II

85 Preparation of 3 - hydroxy - 2,6 - dichlorobenzonitrile

The 3 - acetoxy - 2,6 - dichlorobenzonitrile prepared in Example I (51 w) was hydrolysed by heating for 1 hour on a water-bath with a

Analysis Found: C 44.7; H 1.8; Cl 37.0%  
C<sub>7</sub>H<sub>2</sub>ONCl<sub>2</sub> requires C 44.7; H 1.6; Cl 37.8%

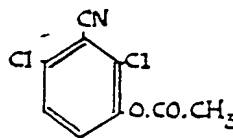
action mixture is then poured into water or aqueous alkali metal carbonate solution. The desired nitrile usually separates as an oil which soon solidifies and can be filtered off. Alternatively, the nitrile can be extracted with ether. The nitrile so obtained contains an acyloxy group in the meta position.

This acyloxy derivative may, if desired, be recrystallised from a solvent, for example, aqueous alcohol, but is in general sufficiently pure for use in subsequent reactions. It may be hydrolysed by warming in an aqueous or preferably aqueous alcoholic medium with an alkali metal hydroxide. Preferably, a homogeneous solution of the acyl derivative and sodium or potassium hydroxide in aqueous alcohol is heated under reflux. The hydrolysis is preferably effected in an inert atmosphere, for example, of nitrogen. The alkali metal phenoxide so obtained may be converted into the free phenol by acidifying, for example, with hydrochloric acid.

The following Examples illustrate the process of the invention. In these Examples, parts by weight (w) and parts by volume (v) bear the same relation as the kilogramme and the litre.

#### EXAMPLE I

Preparation of 3 - acetoxy - 2,6 - dichlorobenzonitrile



3 - Hydroxy - 2,6 - dichlorobenzaldehyde (56 w) was refluxed with acetic anhydride (200 v) for 2 hours. The cooled reaction mixture was poured into cold water, whereupon an oil separated which soon solidified. The acid was neutralised with sodium bicarbonate and the product filtered off (80% yield) and recrystallised from alcohol, giving 51 w of 3 - acetoxy - 2,6 - dichlorobenzonitrile of m.p. 106°C.

slight excess of 3 N potassium hydroxide solution in an atmosphere of nitrogen, after which the solution was filtered and the filtrate, which contained the potassium salt of the substituted phenol, was acidified with concentrated hydrochloric acid.

The hydroxy nitrile which precipitated was filtered off, washed with water, dried and recrystallised from benzene. It had m.p. 196°—8°C. Yield 41 w.

## EXAMPLE III

Preparation of 2 - chloro - 3 - acetoxybenzonitrile and 2 - chloro - 3 - hydroxybenzonitrile

- 5 2 - Chloro - 3 - acetoxybenzonitrile was prepared in a manner analogous to that described in Example I, using 2 - chloro - 3 - hydroxybenzaldehyde as starting material. The product had m.p. 82°—83°C. Yield 75% of theory.

Analysis Found: C 55.4; H 3.2%  
C<sub>8</sub>H<sub>5</sub>O<sub>2</sub>NCl requires C 55.2; H 3.0%

- 15 The acetoxy derivative thus obtained was hydrolysed in a manner analogous to that described in Example II. The product has m.p. 188—189°C. Yield 65% of theory, based on acetyl compound.

Analysis Found: C 55.0; H 2.7%  
C<sub>8</sub>H<sub>5</sub>NCl requires C 54.7; H 2.6%

- 20 The benzonitrile derivatives used in the compositions of the invention are highly toxic to seeds and some are also highly toxic when sprayed on foliage plants. Some compounds exhibit a high degree of selectivity, being selectively toxic to dicotyledonous seeds or plants. Thus, 3 - acetoxy - 2,6 - dichlorobenzonitrile applied as an aqueous dispersion at the rate of 1 pound of the nitrile per acre, to soil containing oat and mustard seeds inhibited the development of practically all the mustard seeds while a dosage of more than 10 pounds per acre was required to obtain the same result with the oat seeds. The corresponding 3 - hydroxy derivative showed less selectivity, 90% inhibition of development of mustard seed being obtained at a dosage of 5.0 pounds per acre and of oat seed at a dosage of 6.0 pounds per acre. Similarly, an aqueous dispersion of 2 - chloro - 3 - hydroxybenzonitrile applied to soil at the rate of 1.2 pounds of the nitrile per acre caused 90% inhibition of development of mustard seeds while a dosage of 6.8 pounds per acre was required to give 90% inhibition of development of oat seeds. The corresponding acetoxy derivative caused 90% inhibition of development of mustard applied 4.0 pounds per acre and of oats at 4.4 pounds per acre, thus showing reduced selectivity and activity. When sprayed on oat, mustard and linseed seedlings, 2 - chloro - 3 - hydroxybenzonitrile and the corresponding acetoxy derivatives were selectively toxic to mustard, causing 90% growth inhibition at dosages to 4.1 and 7.9 pounds per acre respectively while more than 10 pounds per acre were required to effect the same degree of growth inhibition of oat and linseed seedlings. 3 - Hydroxy - 2,4,6 - trichlorobenzonitrile also showed high selective toxicity to mustard seed and caused 90% inhibition of development at a dosage of 4.0 pounds per acre,

while more than 10 pounds per acre was required to cause 90% inhibition of development of oat seeds. This compound also showed high selective toxicity to mustard plants. Thus, an aqueous dispersion of this compound when sprayed on to young oat and mustard plants at the rate of 1 pound per acre, completely inhibited growth of mustard plants, compared with untreated control plants, while a dosage of more than 10 pounds per acre was required to obtain the same result with oat plants. In all these tests, the nitriles were applied as aqueous dispersions prepared from a solution in acetone containing 5.0% by weight of the nitrile and 1.25% by weight of Triton X 155 as dispersing agent ("Triton" is a Registered Trade Mark).

The herbicidal compositions of the invention contain in addition to the above benzonitrile derivatives, a solid carrier or a surface active agent, or a solid or liquid carrier and a surface active agent, or a petroleum hydrocarbon as hereinafter specified.

The compositions of the invention may be formulated as dusts utilising a finely divided solid carrier, e.g. tricalcium phosphate, bentonite, Kieselguhr, a clay of the monimorillonite, kaolinite or attapulgite groups, or a synthetic hydrated silicon oxide or synthetic calcium silicate.

The compositions of the invention may also be formulated as wettable powders comprising a major proportion of the benzonitrile derivative in finely divided form, mixed with a dispersing or deflocculating agent and, if desired, a finely divided solid carrier. Preferably the benzonitrile derivative constitutes at least 10% by weight of such compositions and more preferably, at least 50% by weight of such compositions. The concentration of the dispersing or deflocculating agent should lie in general between 0.1 and 10% by weight of the total composition, though smaller or larger amounts may be used if desired.

The dispersing or deflocculating agent used may be a protective colloid such as gelatin, glue, casein, gums or a synthetic polymeric material such as polyvinyl alcohol. Preferably, however, the dispersing or deflocculating agents used are sodium or calcium salts of high molecular weight sulphonic acids e.g. the sodium or calcium salts of the lignin sulphonic acids derived from sulphite cellulose waste liquors. Calcium or sodium salts of condensed aryl sulphonic acids, such as are available under the trade name "Tamol" are also suitable.

The dispersing or deflocculating agents used may also be non-ionic emulsifiers. Suitable compounds of this type are the condensation products of fatty acids containing at least 12 carbon atoms in the molecule and preferably 16 to 20 carbon atoms in the molecule, abietic acid or naphthenic acids obtained in the refining of petroleum lubricating fractions, with

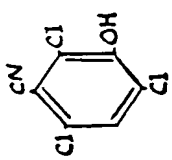
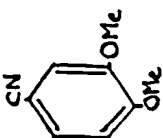
- alkylene oxides such as, for example, the condensation product of oleic acid and ethylene oxide containing 6 ethylene units in the molecule. Partial esters of the above acids with polyhydric alcohols such as glycerol, polyglycerol, sorbitol or mannitol may also be used.
- The dispersing or deflocculating agents referred to above may also possess wetting properties but in general it is preferable to incorporate two separate surface active agents, one having particularly good dispersing or deflocculating properties and the other having particularly good wetting properties. The actual amount or wetting agent incorporated can be varied considerably and lies usually between 0.2 and 10% by weight based on the total composition. Suitable wetting agents include the alkali metal salts of sulphuric acid esters or sulphonic acids, preferably containing at least 10 carbon atoms in the molecule. Thus for example salts of secondary alkyl sulphates or alkyl aryl sulphonates having at least 10 carbon atoms in the alkyl group, especially the sodium salts, for example sodium dodecyl benzene sulphonate. Non-ionic wetting agents may also be employed for example, polyalkylene oxide polymers or condensation products of alkylene oxides with aromatic nuclei (e.g. octyl cresol).
- Granulated compositions comprising a suitable carrier having a benzonitrile derivative incorporated therewith are also included in the invention. These may be prepared by impregnating a granular carrier e.g. of absorbent clay, with the toxicant, or granulating a mixture of a finely divided solid carrier such as is used for preparing dusts and the toxicant. The carrier used may consist of or contain a fertiliser or fertiliser mixture for example, superphosphate.
- The benzonitrile derivatives may also be formulated by intimately mixing them with a solid resinous carrier which is thermoplastic or solvent soluble, for example, a resin or an asphaltite for example, gilsonite, or an asphaltic bitumen. Preferably these compositions are prepared in a granular or pelleted form.
- Compositions of the present invention also comprise the benzonitrile and a petroleum hydrocarbon fraction. Petroleum hydrocarbon fractions which may be used should have a flash point above 73°F, for example a refined aromatic extract of kerosine boiling in the range 145°C to 290°C. The compositions of the present invention may also contain auxiliary solvents such as alcohols, ketones and polyalkylene glycol ethers and esters.
- The liquid compositions of the present invention which are oil solutions are suitable for application by low volume spraying for example at the rate of 5 to 10 gallons per acre. They may be diluted with a cheap solvent for high volume spraying.
- Compositions of the present invention may also be formulated as emulsifiable concentrates which are concentrated solutions or dispersions of the benzonitrile in an organic liquid, preferably a water-insoluble organic liquid, containing an emulsifying or wetting agent. Suitable organic liquids are, for example organic solvents, such as alcohols, ketones, chlorinated hydrocarbons and aromatic hydrocarbons and the petroleum hydrocarbon fractions as described above.
- The concentration of emulsifier will normally be within the limits 0.5% and 25.0% based on the final composition, depending upon the particular emulsifying or dispersing system used.
- Suitable types of emulsifier for use in these emulsions or emulsifiable concentrates are the non-ionic deflocculating and wetting agents described above; also suitable are alkyl aryl sulphonates, long chain alkyl ammonium salts and alkyl sulpho-succinates.
- Concentrates giving rise to water-in-oil emulsions in which the herbicide is in the oil phase may also be used.
- Aqueous dispersions and emulsions, for example, compositions obtained on diluting the wettable powders or emulsifiable concentrates of the present invention with water also lie within the scope of the present invention.
- The compositions of the invention may also include other ingredients, for example, other herbicides, pesticides, acid neutralising stabilizing agents and "stickers."
- The present invention is illustrated by the following Examples.
- EXAMPLE IV
- Herbicidal compositions of the present invention were prepared by dissolving a benzonitrile derivative in acetone to give a 2.5% wt./vol. solution containing 1.25% wt./vol. of Triton X155 as an emulsifying agent. This solution was then diluted with increasing amounts of water to give a range of dispersions varying the concentration of toxicant. The dispersions were applied to soil and plants in volumes to give the required weight of toxicant per unit area (expressed in the Table as pounds per acre).
- The herbicidal activity of these compounds was then tested against two representative seeds, oats, and mustard, sown in sterile soil, the top surface of which was sprayed before emergence of the seedlings and three representative plants, oats, mustard and linseed treated post-emergence when 3 or 4 inches high either with soil drenches in which the soil was saturated with the aqueous dispersions or with foliar sprays. The phytotoxic effect of the compositions were assessed for pre-emergence and post-emergence applications by determining the reduction from the control in fresh weight of stem and leaf of test plants one or two weeks after treatment. The activity of the compositions of the present invention in these tests was expressed as dosage required for 90% inhibition of foliage growth (G.I.D. 90) or the dosage required for 50% inhibition of foliage growth (G.I.D. 50) of the test species. Table I shows the effect on the test species of the compositions prepared as stated above and containing some of the most active compounds.

5 compositions prepared as stated above and containing some of the most active compounds.

TABLE

Benzonitrile derivative formula	50% Growth Inhibition dose lb/acre						90% Growth Inhibition dose lb/acre					
	Seeds			Plants			Seeds			Plants		
	Soil Spray			Foliar Spray			Soil Spray			Foliar Spray		
	O	M		O	M	L	O	M		O	M	L
	1.0	0.6		6.1	1.1	X	2.8	4.8	X	X		
	0.8	<0.6		X	3.4	X	2.8	7.0	X	X		
	2.5	2		X	3.0	X	X			X		
	2.2	1		X	6.6	X	X			X		

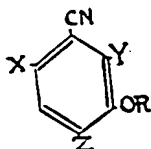
TABLE (cont.)

Benzonitrile derivative formula	50% Growth Inhibition dose lb/acre						90% Growth Inhibition dose lb/acre					
	Seeds			Plants			Seeds			Plants		
	Soil Spray			Foliar Spray			Soil Spray			Foliar Spray		
	O	M		O	M	L	O	M		O	M	L
	6.8	1		5.5	<1	<1	6.8	X	3.0			
								X				
	<3	X		X	X	X	X	7.4	X	X	X	X

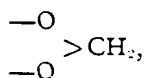
O = Oats    M = Mustard    L = Linseed    X = more than 10 lb/acre.

## WHAT WE CLAIM IS:—

1. A composition suitable for combatting weeds comprising a benzonitrile derivative having the general formula



wherein R represents a hydrogen atom, an alkali metal, an acyl group, a phenyl group, or an alkyl group of 1 to 4 carbon atoms which may be substituted by a carboxyl group or by an alkoxy-carbonyl group; X represents a hydrogen atom, a halogen atom or the group OR<sup>1</sup> wherein R<sup>1</sup> represents a hydrogen atom, an alkali metal, an alkyl group of 1 to 4 carbon atoms or an acyl group; Y represents a hydrogen atom, a halogen atom or a cyano group; Z represents a hydrogen atom, a halogen atom or an alkoxy group of 1 to 4 carbon atoms, or Z and OR together represent a methylene dioxy group



together with a solid carrier, or a surface active agent, or a solid or liquid carrier and a surface active agent, or a petroleum hydrocarbon fraction as hereinbefore defined.

2. A composition as claimed in claim 1 comprising said benzonitrile derivative, a solid or liquid carrier and a surface active agent.

3. A composition as claimed in claim 1 or 2 wherein said alkali metal is sodium or potassium.

4. A composition as claimed in any one of claims 1 to 3 wherein said acyl groups are derived from an aliphatic carboxylic acid of 1 to 4 carbon atoms.

5. A composition as claimed in claim 4 wherein said acid is acetic acid.

6. A composition as claimed in any one of the preceding claims wherein the alkyl group is a methyl group.

7. A composition as claimed in any one of the preceding claims which is a dust comprising said benzonitrile derivative and a finely divided solid carrier.

8. A composition as claimed in any one of claims 1 to 6 which is a wettable powder comprising said benzonitrile derivative and a dispersing or deflocculating agent.

9. A composition as claimed in claim 8 containing also a finely divided solid carrier.

10. A composition as claimed in claim 8 or 9 containing also a wetting agent.

11. A composition claimed in any one of claims 1 to 6 in the form of granules or

pellets and comprising said benzonitrile derivative and a solid carrier.

12. A composition as claimed in claim 11 wherein said carrier consists of or comprises a fertiliser.

13. A composition as claimed in any one of claims 1 to 6 or 11 comprising said benzonitrile derivative and a thermoplastic or solvent soluble solid resinous carrier.

14. A composition as claimed in any one of claims 1 to 6 or 14 wherein said petroleum fraction is a refined aromatic extract of kerosine.

15. A composition as claimed in any one of claims 1 to 6 which is an emulsifiable concentrate comprising a solution or dispersion of said benzonitrile derivative in an organic liquid containing an emulsifying or wetting agent.

16. A composition as claimed in claim 15 wherein said organic liquid is the petroleum fraction claimed in claim 14.

17. A composition as claimed in any one of claims 1 to 6 which is an aqueous dispersion or emulsion.

18. A composition as claimed in claim 17 which is obtained by diluting the compositions claimed in any one of claims 8 to 10 or 15 or 16 with water.

19. 2 - Chloro - 3 - hydroxybenzonitrile.

20. 2 - Chloro - 3 - acetoxybenzonitrile.

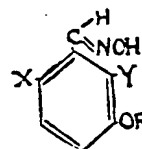
21. 2,6 - Dichloro - 3 - hydroxybenzonitrile.

22. 2,6 - Dichloro - 3 - acetoxybenzonitrile.

23. A composition claimed in any one of claims 1 to 18 containing a compound claimed in any one of claims 19 to 22.

24. Compositions as claimed in any one of claims 1 to 18 or 23 substantially as hereinbefore described with reference to Example IV.

25. A process for preparing a compound claimed in any one of claims 19 to 22 which comprises treating a benzaldoxime of formula



wherein X represents a hydrogen or halogen atom, Y represents a halogen atom and R represents a hydrogen atom or an acetyl group, with a dehydrating agent.

26. A process as claimed in claim 25 wherein the dehydrating agent is acetyl chloride or acetic anhydride.

27. A process as claimed in claim 25 or 26 substantially as hereinbefore described with reference to Examples I to III.

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Agents for the Applicants.

## PROVISIONAL SPECIFICATION

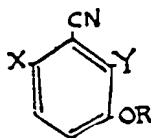
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# Novel Compounds for use as Herbicides and in Herbicidal Compositions

We, "SHELL" RESEARCH LIMITED, a British Company of St. Helens Court, Great St. Helens, London, E.C.3, do hereby declare this invention to be described in the following statement:—

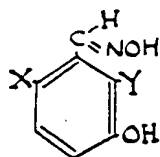
This invention is concerned with novel benzonitrile derivatives, useful as intermediates and herbicides, and to a process for their preparation.

The novel compounds of the invention have the general formula



wherein R represents a hydrogen atom, the hydrogen equivalent of a metal, or an acyl group of 1 to 10 carbon atoms; X represents a hydrogen or a halogen atom or the group OR<sup>1</sup> wherein R<sup>1</sup> represents a hydrogen atom, or the hydrogen equivalent of a metal, an alkyl group of 1 to 4 carbon atoms or an acyl group of 1 to 10 carbon atoms, and Y represents a halogen atom.

The novel compounds of the invention can be prepared by treating a benzaldoxime of formula



with a dehydrating agent which will remove the elements of water from the aldoxime group. Suitable dehydrating agents for this purpose are acid chlorides or acid anhydrides, especially acetyl chloride and acetic anhydride. Preferably the aldoxime and the acid chloride or acid anhydride, preferably in excess, are heated together under reflux. In general, the reaction is complete in about four to five hours. Shorter reaction times may be employed but the products obtained are less pure. The reaction mixture is then poured into water or aqueous alkali metal carbonate solution. The desired nitrile usually separates as an oil which soon solidifies and can be filtered off. Alternatively, the nitrile can be extracted with ether. The nitrile so obtained contains an acyloxy group in the meta position.

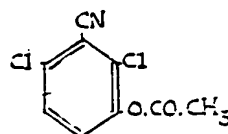
This acyloxy derivative may, if desired, be

recrystallised from a solvent, for example, aqueous alcohol, but is in general sufficiently pure for use in subsequent reactions. It may be hydrolysed by warming in an aqueous or preferably aqueous alcoholic medium with an alkali or alkaline earth metal hydroxide. Preferably, a homogeneous solution of the acyl derivative and sodium or potassium hydroxide in aqueous alcohol is heated under reflux. The alkali or alkaline earth metal phenoxide so obtained may be converted into the free phenol by acidifying, for example, with hydrochloric acid.

The following Examples illustrate the process of the invention. In these Examples, parts by weight (w) and parts by volume (v) bear the same relation as the kilogramme and the litre.

## EXAMPLE I

Preparation of 3 - acetoxy - 2:6 - dichlorobenzonitrile



3 - Hydroxy - 2:6 - dichlorobenzaldoxime (56 w) was refluxed with acetic anhydride (200 v) for 2 hours. The cooled reaction mixture was poured into cold water, whereupon an oil separated which soon solidified. The acid was neutralised with sodium bicarbonate and the product filtered off (80% yield) and recrystallised from alcohol, giving 51 w of 2:6 - dichloro - 3 - acetoxy benzonitrile of m.p. 106°C.

Found: C 46.7; H 2.3; Cl 30.7%  
C<sub>7</sub>H<sub>2</sub>O<sub>2</sub>NCl requires C 46.9; H 2.2; Cl 30.9%

In other similar preparations, the product was extracted with ether from the aqueous reaction mixture.

## EXAMPLE II

Preparation of 3 - hydroxy - 2:6 - dichlorobenzonitrile

The 3 - acetoxy - 2:6 - dichlorobenzonitrile prepared in Example I (51 w) was hydrolysed by heating for 1 hour on a water bath with a slight excess of 3 N potassium hydroxide solution after which the solution was filtered and the filtrate acidified with concentrated hydrochloric acid.

The hydroxy nitrile which precipitated was filtered off, washed with water, dried and re-

crystall  
1962—

Found:  
C,H,O

We,  
British  
St. He  
this in  
statem  
The  
compo  
which,  
seeds,  
is also  
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crystallised from benzene. It then had m.p. 196°—8°C. Yield 41 w.

Found: C 44.7; H 1.8; Cl 37.0%,  
C<sub>2</sub>H<sub>3</sub>ONCl<sub>2</sub> requires C 44.7; H 1.6; Cl 37.8%,

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London, E.C.3.

# PROVISIONAL SPECIFICATION

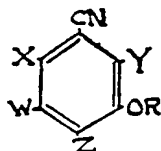
No. 129 A.D. 1960

## Herbicidal Compositions and Novel Compounds for use therein

5 We, "SHELL" RESEARCH LIMITED, a British Company, of St. Helen's Court, Great St. Helen's, London, E.C.3, do hereby declare this invention to be described in the following statement:—

10 The present invention is concerned with compositions for use as herbicides, some of which, being toxic to dormant and germinating seeds, are useful as pesticides. This invention is also concerned with a method of inhibiting plant growth by the application of the compositions of the invention to plants or seeds and with the treatment of soil with the compositions of the invention. This invention is also concerned with novel compounds having herbicidal properties for use in said compositions.

The present invention provides a herbicidal composition comprising a benzonitrile derivative having the general formula



wherein R represents a hydrogen atom, the hydrogen equivalent of a metal, or an acyl group of 1 to 10 carbon atoms, or a methyl group;

30 X represents a hydrogen or a halogen atom or the group OR<sup>1</sup> wherein R<sup>1</sup> represents a hydrogen atom, or the hydrogen equivalent of a metal, an alkyl group of 1 to 4 carbon atoms or an acyl group of 1 to 10 carbon atoms, or a methoxy group;

35 Y represents a halogen atom;

W and Z each represent a hydrogen or a halogen atom or an alkyl group of 1 to 4 carbon atoms.

40 In the above general formula, the halogen is preferably chlorine or bromine. R and R<sup>1</sup> may each represent the hydrogen equivalent of a metal which may be an alkali metal, preferably sodium, or an alkaline earth metal, preferably calcium.

45 The acyl group which R and R<sup>1</sup> may represent is the radical of an organic acid, preferably of a carboxylic acid, though acyl radicals from sulphonic acids and phosphorus-contain-

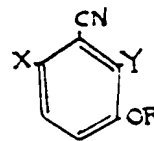
ing acids may also be used. The acids may be acyclic or cyclic and saturated or unsaturated. Preferred acids are acetic, propionic, butyric, benzoic and toluic acids.

Examples of compounds of the above general formula are:—

3 - hydroxy - 2:6 - dichlorobenzonitrile  
3 - acetoxy - 2:6 - dichlorobenzonitrile  
3 - hydroxy - 2:4:6 - trichlorobenzonitrile  
3 - benzoxy - 2:4:6 - trichlorobenzonitrile  
3:6 - diacetoxy - 2 - chlorobenzonitrile  
3:6 - diacetoxy - 2:4 - dichlorobenzonitrile  
3:6 - diacetoxy - 2:4:5 - trichlorobenzonitrile  
3 - methoxy - 2:6 - dichlorobenzonitrile  
3:6 - dimethoxy - 2 - chlorobenzonitrile

as well as the corresponding bromo derivatives obtained by replacing one or more of the chlorine atoms by bromine atoms, and the sodium, potassium and calcium salts of the hydroxy compounds.

A class of compounds broadly defined by the above general formula but having the structure



wherein X, Y and R have the aforesaid meanings are believed to be novel. Their preparation is described in copending application No. 130/60. Compounds of this formula obtained when X and Y each represent a halogen atom, preferably a chlorine or bromine atom, or when X represents a group OR where R represents a hydrogen atom, the hydrogen equivalent of a metal or an acyl group and Y represents a halogen atom, preferably a chlorine or bromine atom, have particularly good herbicidal activity and are preferred compounds for use in the compositions of the invention.

The benzonitrile derivatives used in the compositions of the invention are highly toxic to seeds and some are also highly toxic when sprayed on foliage plants. Some compounds inhibit a high degree of selectivity, being selectively toxic to di - coryledonous seeds or

plants. Thus, 3 - acetoxy - 2:6 - dichloro-  
benzonitrile applied as an aqueous dispersion  
containing Triton X155 ("Triton" is a Regis-  
tered Trade Mark) as dispersing agent at the  
rate of 1 pound of the nitrile per acre, to soil  
containing oat and mustard seeds completely  
inhibited the germination of the mustard seed  
while a dosage of more than 10 pounds per acre  
was required to obtain the same result with  
the oat seeds. The corresponding 3 - hydroxy  
derivative showed less selectivity, the germina-  
tion of mustard seed being completely inhibited  
at a dosage of 5.0 pounds per acre and of oat  
seed at a dosage of 6.0 pounds per acre. 3 -  
hydroxy - 2:4:6 - trichlorobenzonitrile also  
showed high selective toxicity to mustard seed  
whose germination was completely inhibited at  
a dosage of 4.0 pounds per acre, while more  
than 10 pounds per acre was required to inhibit  
germination of oat seeds completely. This com-  
pound also showed high selective toxicity to  
mustard plants. Thus, an aqueous dispersion  
of this compound when sprayed on to young  
oat and mustard plants at the rate of 1 pound  
per acre, completely inhibited growth of mus-  
tard plants, compared with untreated control  
plants, while a dosage of more than 10 pounds  
per acre was required to obtain the same result  
with oat plants.

The herbicidal compositions of the inven-  
tion contain in addition to the above benzo-  
nitrile derivatives, a solid carrier compatible  
therewith, or a surface active agent, or both a  
solid carrier and a surface active agent. The  
invention further provides herbicidal composi-  
tions comprising compounds of the above  
general formulae together with a petroleum  
hydrocarbon fraction and emulsifiable concen-  
trates comprising a solution or dispersion of a  
benzonitrile derivative of the above general  
formulae in an organic solvent, for example,  
in a petroleum hydrocarbon fraction, and an  
emulsifying agent.

The compositions of the invention may be  
formulated as wettable powders comprising a  
major proportion of the benzonitrile derivative,  
preferably at least 80% by weight thereof, in  
finely divided form, mixed with a dispersing  
or deflocculating agent. Alternatively, the wet-  
table powders comprise the benzonitrile deriva-  
tive, a finely divided solid carrier as described  
above for use in preparing dust compositions  
and a dispersing or deflocculating agent. Pre-  
ferably the benzonitrile derivative constitutes  
at least 10% by weight of such compositions  
and more preferably, at least 50% by weight  
of such compositions. The concentration of the  
dispersing or deflocculating agent should be  
sufficient to enable the wettable powder to be  
readily dispersed in water for the production  
of an aqueous dispersion for application, for  
example, by spraying and for this purpose, in  
general between 0.2 and 10% by weight of the  
total composition is satisfactory although the  
actual amount required will depend upon the

nature of the dispersing agent or deflocculating  
agent and the nature of the carrier and benzo-  
nitrile derivative used. Preferably, the amount  
of deflocculating agent or dispersing agent used  
should be sufficient to give a suspensibility of  
at least 25% by weight and preferably of at  
least 55% in the following suspensibility test:

#### TEST FOR SUSPENSIBILITY

A sample of wettable powder containing a  
previously determined amount of pesticide is  
mixed with water to give 250 ml of suspension  
in a 250 ml. graduated cylinder of height 21  
cm. between the 0 and 250 ml. marks. The sus-  
pension is allowed to stand undisturbed for 30  
minutes. Nine-tenths by volume of the suspen-  
sion is then removed by suction without dis-  
turbance any precipitate which may have sep-  
arated and the amount of pesticide in the re-  
mainder of the suspension is determined. The  
suspensibility is then calculated from the fol-  
lowing formula:

$$\text{Suspensibility, \% wt.} = \frac{(b - a)}{b} \times \frac{1000}{9}$$

where a is the weight of the pesticide found  
in the final 25 mls of suspension.

b is the weight of pesticide in the sample used  
to prepare the suspension.

The dispersing or deflocculating agent used  
in the compositions of the invention may be  
any substance having definite dispersing or  
deflocculating properties as distinct from wet-  
ting properties, although these substances may  
also possess wetting properties.

The deflocculating agent used may be a  
protective colloid such as gelatin, glue, casein,  
gums or a synthetic polymeric material such as  
polyvinyl alcohol. Preferably, however, the de-  
flocculating agents used are certain commer-  
cially available products which are sodium or  
calcium salts of high molecular weight sul-  
phonic acids e.g. the sodium or calcium salts of  
the lignin sulphonic acids derived from sul-  
phite cellulose waste liquors and known, for  
example, as Goulac (Registered Trade Mark)  
or "Penex" sulphite lye. The calcium or  
sodium salts of condensed aryl sulphonic acids,  
such as are available under the trade names of  
"Leukanol," "Intraphore" and "Tamol" are  
also suitable.

The dispersing or deflocculating agents used  
may also be non-ionic emulsifiers. Suitable  
compounds of this type are the condensation  
products of fatty acids containing at least 12  
carbon atoms in the molecule and preferably  
16 to 20 carbon atoms in the molecule, abietic  
acid or naphthenic acids obtained in the refin-  
ing of petroleum lubricating fractions, with  
alkylene oxides such as ethylene oxide or  
propylene oxide or with both ethylene oxide  
and propylene oxide as, for example, the con-  
densation product of oleic acid and ethylene  
oxide containing 6 ethylene units in the mole-

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cule which is available under the trade name of Estax 37 (the word Estax is a Registered Trade Mark). Similar products are obtained by esterifying the above-mentioned acids with polyglycols. Partial esters of the above acids with polyhydric alcohols such as glycerol, polyglycerol, sorbitol or mannitol may also be used. Examples of such compounds are pentaerythritol glycerol oleate, which is available under the name of Estax 29 and pentaerythritol distearate, which is available as Estax 2.

The dispersing or deflocculating agents referred to above may also possess wetting properties but in general it is preferable to incorporate two separate surface active agents, one having particularly good dispersing or deflocculating properties and the other having particularly good wetting properties. The actual amount of wetting agent incorporated will depend upon the other components present in the composition and especially on the dispersing or deflocculating agent, but usually an amount between 0.2 and 10%, by weight based on the total composition is suitable. Preferably the amount of wetting agent incorporated is just sufficient to permit the composition to be completely wetted in not more than one minute in the following wetting test:—

In this test, 5 grams of the composition are added without agitation to 100 ml. of hard water (hardness equivalent to 342 ppm of calcium carbonate) contained in a 250 ml. beaker of 6.5 cm. diameter and the time taken for the powder to be wetted completely is noted.

Larger proportions of the wetting agent may be used but should not be such as to reduce materially the weathering properties of the deposit obtained when the aqueous compositions are sprayed on plants or soil.

Wetting agents are well known in the art. Suitable wetting agents include the alkali metal salts of sulphuric acid esters or sulphonic acids, preferably containing at least 10 carbon atoms in the molecule. Thus for example long chain alkyl sulphates such as sodium lauryl sulphate or aliphatic or aromatic sulphonates such as sulphonated castor oil or various alkyl aryl sulphonates especially the sodium salts of alkyl aryl sulphonates having at least 10 carbon atoms in the alkyl group such as for example sodium dodecyl benzene sulphonate, Sipex N.S.L., Tensopol U.S.P. and Empicol L.Z. Non-ionic wetting agents may also be employed for example, polyalkylene oxide polymers, e.g. the "Pluronic," high molecular weight alkyl polyglycol ethers or analogous thioethers such as decyl, dodecyl, and tetradecyl polyglycol ethers and thioethers containing from 25—75 carbon atoms. Condensation products of polyalkylene oxides with aromatic nuclei (e.g. octyl cresol), such as Triton X100, Nonidet P.40 are also suitable. (The words "Empicol," "Pluronic," "Triton" and "Nonidet" are Registered Trade Marks.)

Granulated compositions comprising a suitable carrier having a benzonitrile derivative incorporated therewith are also included in the invention. A carrier such as is used for preparing dusts and wettable powders as described above may be used for this purpose or it may consist of or contain a fertiliser or fertiliser mixture, for example, superphosphate. The granules may be prepared by intimately mixing the benzonitrile derivative with the carrier and feeding the mixture into a rotating drum where it is sprayed with a small quantity of water sufficient to cause the particles to agglomerate and form granules which are then, passed to a rotary drier. Alternatively, the carrier can be mixed with the benzonitrile derivative in organic solvent solution or preferably, as an aqueous dispersion and the mixture then fed into a rotary drier which dries and simultaneously rolls the particles into granules, or the carrier can be fed into a rotating drum and therein sprayed with a small quantity of an aqueous dispersion or solvent solution of a benzonitrile derivative and the resulting granules then passed into a drier.

The benzonitrile derivatives may also be formulated by intimately mixing them with a solid resinous carrier which is thermoplastic or solvent soluble as described in copending application 9206/59 (Serial No. 898,915). The resinous carrier may, for example, be a resin or an asphaltite such as, for example, gilscrite. Preferably these compositions are formulated as granules.

Compositions of the present invention also comprise the benzonitrile and a petroleum hydrocarbon fraction. Petroleum hydrocarbon fractions which may be used should have a flash point above 73°C. Suitable fractions include lubricating oils, fuel oils and kerosene and particularly the extract obtained in the Edeleanu treatment of kerosene and which contains at least 56% by weight of aromatics. This solvent which is available under the Registered Trade Mark "Karex" has a distillation range of 175°C. to 290°C. Another very suitable solvent is that available under the Registered Trade Mark "Octaro." This is a refined kerosene extract having a boiling range between 145°C and 200°C and an aromatic content of at least 80%, by weight. Other suitable hydrocarbon solvents include for example petroleum xylenes. The compositions of the present invention may also contain auxiliary solvents such as alcohols, ketones and polyalkylene glycol ethers and esters.

The liquid compositions of the present invention which are oil solutions are suitable for application by low volume spraying for example at the rate of 5 to 10 gallons per acre. They may also be diluted with a cheap solvent for high volume spraying.

Compositions of the present invention may also be formulated as emulsifiable concentrates which are concentrated solutions or dispersions

of the benzonitrile in an organic liquid, preferably a water-insoluble organic liquid, containing an added emulsifying and/or wetting agent. These concentrates may also contain a proportion of water for example up to 50% by volume, based on the total composition (i.e. a "mayonnaise" composition) to facilitate subsequent dilution with water. Suitable organic liquids are for example the petroleum hydrocarbons as described above. These concentrates may be diluted with large volumes of water for application for higher volume spraying.

The amount of the emulsifier used will depend upon the particular emulsifying or dispersing system used but the concentration of emulsifier will normally be within the limits 0.5% and 25.0% based on the final composition. It should be sufficient to provide an emulsifiable concentrate which will satisfy the following test:—

#### EMULSIFIER TEST

5 ml. of the emulsifiable concentrate is diluted with 95 ml. of hard water (total of 342 p.p.m. of calcium carbonate) in a stoppered measuring cylinder. After one inversion the sample should have dispersed completely. The cylinder and the contents are inverted a further 29 times (total of 30 inversions) and then allowed to stand at room temperature. After two hours standing there should be no oil separation.

Suitable types of emulsifier for use in these emulsions or emulsifiable concentrates are the nonionic deflocculating agents described above, polyalkylene oxide condensate products with aromatic nuclei (e.g. with phenols), long-chain aliphatic alcohols or acids (e.g. lauryl and cetyl alcohols or acids), amines (e.g. the Ethomeens), amides (e.g. Ethamids), vegetable oils, sucrose esters and sorbitan esters (e.g. Sorbester); also suitable are alkyl aryl sulphates, long chain alkyl ammonium salts and alkyl sulpho-succinates (e.g. Aerosol OT). (The words "Ethomeens," "Ethomids" and "Sorbester" are Registered Trade Marks.)

Concentrates giving rise to water-in-oil emulsions may also be used. Advantageously such compositions are formulated with an organic solvent of high volatility and an emulsifier producing on dilution with water in an amount from five to ten times the volume of the concentrate, a water-in-oil type emulsion with the herbicide in the oil phase, suitable for application by low volume spraying.

The dilute compositions obtained on diluting the wettable powders or emulsifiable concentrates of the present invention with water also lie within the scope of the present invention.

These compositions may include the so-called "stickers."

The actual method of preparing the formu-

lation will vary according to the type of formulation required. Thus for example if an emulsifiable concentrate is required the benzonitrile may be mixed with the oil and the emulsifying or dispersing agent added; the production can then readily be emulsified by agitating with the required quantity of water. Similarly if a wettable powder is to be formulated the benzonitrile is preferably mixed with the finely divided solid filler as described above and the dispersing and/or wetting agent added to give a wettable powder which may then be readily dispersed by agitating a liquid carrier such as for example water immediately before spraying. Such a wettable powder can be prepared by grinding a mixture of the benzonitrile solid filler and dispersing and/or wetting agent in a hammer-mill, air-jet mill, pin-mill or other suitable milling equipment.

The compositions of the present invention which comprise the benzonitrile derivative together with a solid carrier preferably also comprise a stabilizer and preferably an acid neutralizing stabilizer. The purpose of such a stabilizer is to reduce the possibility of decomposition of the biologically active material as a result of interaction which carriers having an intrinsic acidity. Suitable acid neutralizing stabilizers are described in Specification 772,193 and include for example ethanolamine, urea, ammonium bicarbonate and hexamethylene tetramine. The stability of the formulation may also be increased by the addition of glycols, polyglycols or alcohols, for example, diacetone alcohol or isopropyl alcohol.

The present invention is illustrated by the following Examples.

#### EXAMPLE I

Herbicidal compositions of the present invention were prepared by dissolving a benzonitrile derivative in acetone to give a 2.5% wt./vol. solution containing 1.25% wt./vol. of Triton X155 as an emulsifying agent. This solution was then diluted with increasing amounts of water to give a range of dispersions varying the concentration of toxicant. The dispersions were applied to soil and plants in volumes to give the required weight of toxicant per unit area (expressed in the Table as lbs. per acre).

The herbicidal activity of these compounds was then tested against two representative seeds, oats and mustard, sprayed pre-emergence and three representative plants, oats, mustard and linseed treated post-emergence when 3 or 4 inches high with soil drenches. The phytotoxic effect of the compositions were assessed for pre-emergence and post-emergence applications by determining the reduction from the control in fresh weight of stem and leaf of test plants one or two weeks after treatment. The activity of the compositions of the present invention in these tests was

expressed as dosages required for 90% inhibition of foliage growth (G.I.D. 90) or the dosage required for 50% inhibition of foliage growth (G.I.D. 50) of the test species. Table I shows the effect of the compositions prepared as stated above on the test species.

TABLE

Name	50% Growth Inhibition dose lb/acre						90% Growth Inhibition dose lb/acre					
	Seeds			Plants			Seeds			Plants		
	Soil Spray			Foliar Spray			Soil Spray			Foliar Spray		
	O	M	<1	O	M	L	O	M	L	O	M	L
3-Acetoxy-2:6-dichloro	<2			X	6.6	X	X	<1	X	X	X	X
3-Hydroxy-2:6-	2.5	<2		X	3.0	X	X	6.0	5.0	X	X	X
3-Hydroxy-2:4:6-trichloro	6.8	<1		5.5	<1	6.8	X	4.0	<1	X	X	6.5

O = Oats    M = Mustard    L = Linseed    X = more than 10 lb/acre

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